Synthesis, Crystal Structure, and Stereochemical Non-rigidity of μ-[1-σ:1—2-η-2-Carboxylato-1-ethylbut-1-enyl-*O*(2Fe)]-bis(tricarbonyliron) (*Fe–Fe*), a New Complex obtained from Iron Carbonyls under Apolar Conditions

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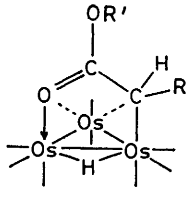
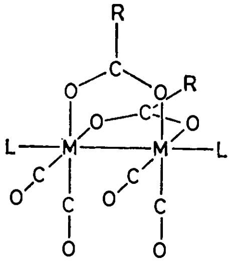
The title complex $[Fe_2(CO)_6\{CEt{=}CEt(CO_2)\}]$ has been obtained from $[Fe_3(CO)_{12}]$ and hex-3-yne in hydrocarbon solvents and characterized by i.r., mass, and ^1H and ^{13}C n.m.r. spectra. The crystal structure has been determined by *X*-ray diffraction methods. The crystals are triclinic, space group $P\bar{1}$, with $Z = 2$, in a unit cell of dimensions $a = 9.500(9)$, $b = 10.627(11)$, $c = 9.140(9)$ Å, $\alpha = 109.61(8)$, $\beta = 117.27(8)$, and $\gamma = 79.71(7)°$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.027$ for 3 295 observed reflections. The complex is formed by two non-equivalent iron atoms (Fe–Fe 2.438 Å), both co-ordinated by three terminal CO, and by a diethyl-substituted ' acrylate ' ligand bound to both irons *via* Fe–C π and Fe–C and Fe–O σ bonds. This ligand is derived by insertion of a CO_2 group between the alkyne and the metal atoms. In the complex an unusual five atom carbon–oxygen–iron heterocycle is present and an oxygen of the carboxyl group symmetrically bridges both iron atoms (Fe–O 1.950 and 1.990 Å). Variable-temperature ^{13}C n.m.r. studies in solution show localized exchange of the CO groups at lower temperatures, whereas at room temperature a bonding interchange within the organic moiety and the iron atoms is proposed. Some comments on the factors influencing the formation of this complex and on the possible intermediates in the reaction are made.

TREATMENT of $[Fe_3(CO)_{12}]$ with alkynes RC_2R and HC_2R yields a considerable variety of tetra- and tri-nuclear complexes,[1-6] and also bi- and mono-nuclear derivatives; in the last derivatives, CO groups often participate in the formation of the organic moiety. Thus CO groups can insert as ketonic groups between two alkynes,[7-10] or between the metals and the organic assembly,[11,12] as well as bridge two or more alkyne molecules and the metals using both the carbon and oxygen atoms.[13-15]

We now report the synthesis, the crystal structure, and the fluxionality of a new complex, $[Fe_2(CO)_6\{CEt{=}CEt(CO_2)\}]$ (1), characterized by a CO_2 group inserted between one alkyne molecule and the iron atoms. Complexes containing CO_2 or CO_2R groups bonded to metals have already been reported. A binuclear cobalt complex bridged by a carbon atom of a lactone ring, obtained in an apolar solvent at high temperature under CO pressure, has been described.[16] Also a variety of osmium [structures (A)—(C)] and manganese derivatives



(A)



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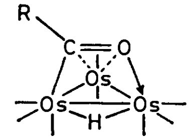

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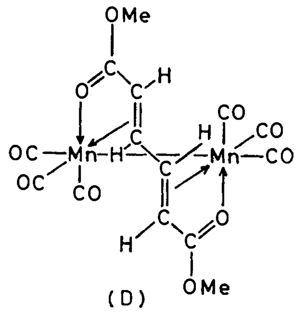
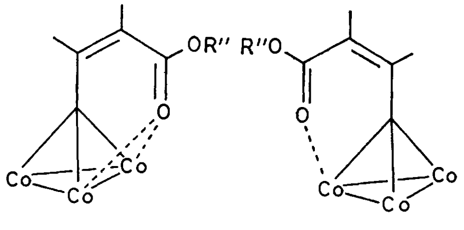
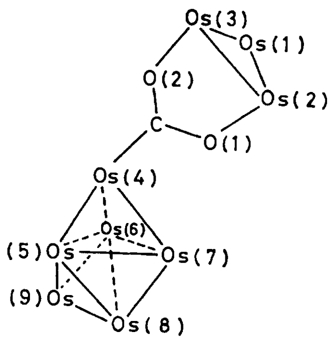


(D)



(E)



(F)

[structure (D)] is known with bridging CO_2R and COR groups;[17-20] an interaction between the CO_2R group and the metals has been revealed, by i.r. methods, in $[Co_3(CO)_9\{CCH{=}CR(CO_2R)\}]$ [proposed structures (E)].[21] Noteworthy also is the anion $[Os_9(CO)_{27}(CO_2)H]^-$ [structure (F)] [22] in which CO_2 bridges three metals *via* one Os–C and two Os–O bonds; presumably, the triply bridging CO_2 is formed by C–O bond breaking in a terminal CO group.

Our complex (1) is obtained by treating $[Fe_3(CO)_{12}]$ with hex-3-yne in refluxing n-heptane, under nitrogen, whereas the above complexes were obtained in polar solvents, and starting with polar reactants or with molecules containing CO_2R groups. Thus (1) can be considered to be an example of activation of CO groups under mild and apolar conditions.

EXPERIMENTAL

Synthesis and Purification of μ-[1-σ : 1—2-η-2-*Carboxylato*-1-*ethylbut*-1-*enyl*-O(2*Fe*)]-*bis*(*tricarbonyliron*) (Fe–Fe), $[Fe_2(CO)_6\{CEt{=}CEt(CO_2)\}]$ (1).—The complex was obtained in 2% yield (with respect to the starting iron carbonyl) by treating $[Fe_3(CO)_{12}]$ with hex-3-yne in a 1 : 2 mol ratio in refluxing n-heptane for 45 min, under a dry nitrogen atmosphere. (The solvent was dried over sodium; hex-3-yne was purchased from K & K Labs. and used without purification. The iron carbonyl, obtained by literature methods,[23] was stored under nitrogen, and contained traces of moisture as well as of n-heptane.) The reaction mixture was filtered and the solvent removed under reduced pressure; the residue was extracted with $CHCl_3$ and separated on t.l.c. plates (Kieselgel P.F.; eluant, diethyl ether–light petroleum mixtures). Other products from the above reaction are $[Fe_3(CO)_9(C_2Et_2)]$ (2) [24] (15% yield), $[Fe(CO)_6(C_2Et_2)_2]$ (3) [25] (15% yield), $[Fe_3(CO)_8(C_2Et_2)_2]$,[26] $[Fe_2(CO)_5\{(C_2Et_2)_3(CO)\}]$ and $[Fe_2(CO)_6\{(C_2Et_2)_3\}]$[27] (all in *ca.* 3% yield), and $[Fe_2(CO)_6\{(C_2Et_2)_2(CO)\}]$ (4) [25] (20% yield); some other products have not yet been identified. Complex (1) was crystallized from n-heptane at 0 °C: the crystals were redissolved in n-heptane and recrystallized at −4 °C (Found: C, 39.1; H, 2.6; Fe, 27.4; O, 30.9. Calc. for $C_{13}H_{10}Fe_2O_8$: C, 38.45; H, 2.50; Fe, 27.5; O, 31.5%).

Since small quantities of (1) were recovered from the mother liquors of the crystallization of (2) after careful purification, we have taken into account that (2) could be an intermediate in the formation of (1).

Other Reactions.—Heating (2) under reflux under a stream of N_2, O_2, or CO_2 or in the presence of distilled water (1 cm^3) (light petroleum, 60 and 90 min; n-heptane, 105 min; and light petroleum, 120 min, respectively) yielded *ca.* 2% of (1); when CO was slowly passed over the solution (light petroleum, 60 min) a 6% yield of (1) was obtained. Heating (3) (n-heptane, 150 min) under reflux under CO_2, or of (4) (light petroleum, 120 min) under O_2, did not yield (1). Thus, only CO is effective in promoting the formation of (1), although independently of its concentration.

Spectra.—The i.r. spectrum of (1) was recorded in an n-heptane solution on a Beckman IR-12 instrument (KBr optics, CO as calibrant). The following absorptions in the CO stretching region were observed: 2 087s, 2 054vs, 2 017vs (sh), 2 010vs, 1 988s, 1 744m—s, and 1 698m—w cm^{-1}. The mass spectrum was obtained on a Varian CH-5 instrument, operating at 70 eV:* the parent ion (*m*/*e* 406) was observed as well as the loss of CO groups. A complete discussion of the fragmentation of the complex will be reported elsewhere.[28] The ^1H n.m.r. spectrum was recorded on a JEOL C 60 HL instrument, in CCl_4 solution: signals at τ 7.42(q), 8.64(t), 8.67(q), and 9.05(t), indicative of different CH_2 and CH_3 groups, were observed. Variable-temperature ^{13}C n.m.r. spectra were obtained on a JEOL PS 100 FT instrument, operating at 25.1 MHz in the Fourier-transform mode: solvents used were CH_2Cl_2–$CDCl_3$ (3 : 1 v/v) at low and room temperature, and $[^2H_8]$toluene at high temperature.

Crystal Data.—$C_{13}H_{10}Fe_2O_8$, $M = 405.91$, Triclinic, $a = 9.500(9)$, $b = 10.627(11)$, $c = 9.140(9)$ Å, $\alpha = 109.61(8)$, $\beta = 117.27(8)$, $\gamma = 79.71(7)°$, $U = 772(1)$ Å^3, $Z = 2$, $D_c = 1.75$ g cm^{-3}, $F(000) = 408$, Mo-K_α radiation, $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) = 19.14 cm^{-1}, space group $P\bar{1}$ from the structure determination.

Unit-cell dimensions, initially determined from rotation and Weissenberg photographs, were subsequently refined by least-squares fit to 18 θ values carefully measured on a Siemens AED single-crystal diffractometer. A dark pink prismatic crystal (dimensions 0.30 × 0.35 × 0.40 mm) was selected for data collection and aligned with its *b* axis parallel to the φ axis of the diffractometer. A total of 3 937 independent reflections (with θ in the range 3—29°) was measured at room temperature using the ω—2θ scanning technique and zirconium-filtered Mo-K_α radiation; 3 295 of these were used in the structure analysis since their intensities were greater than twice their standard deviations (from counting statistics). The intensity data were correc-

TABLE 1

Fractional atomic co-ordinates (×10^4 for Fe, O, and C; ×10^3 for H) with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*
Fe(1)	3 917(1)	2 642(1)	408(1)
Fe(2)	3 320(1)	1 894(1)	−2 641(1)
O(1)	6 867(3)	3 421(3)	743(4)
O(2)	5 312(4)	1 985(4)	3 686(3)
O(3)	3 218(4)	5 404(3)	1 985(4)
O(4)	1 040(3)	201(3)	−5 815(3)
O(5)	3 017(4)	4 123(3)	−3 966(4)
O(6)	6 261(3)	915(3)	−3 082(4)
O(7)	3 812(2)	787(2)	−1 134(3)
O(8)	2 333(3)	−449(2)	−804(4)
C(1)	5 715(4)	3 062(3)	524(4)
C(2)	4 754(4)	2 221(4)	2 424(4)
C(3)	3 511(4)	4 325(4)	1 370(4)
C(4)	1 948(4)	851(3)	−4 604(4)
C(5)	3 124(4)	3 249(4)	−3 455(4)
C(6)	5 154(4)	1 289(4)	−2 889(4)
C(7)	1 747(3)	2 628(3)	−1 735(3)
C(8)	1 580(3)	1 845(3)	−861(4)
C(9)	2 522(3)	584(3)	−950(4)
C(10)	321(4)	1 987(4)	−243(5)
C(11)	904(6)	2 192(7)	1 635(5)
C(12)	606(4)	3 789(3)	−2 161(4)
C(13)	−795(5)	3 335(5)	−3 909(6)
H(101)	−56(4)	281(4)	−49(4)
H(102)	−32(4)	110(4)	−90(5)
H(111)	−9(4)	222(4)	187(4)
H(112)	126(5)	294(4)	213(5)
H(113)	171(4)	139(4)	187(5)
H(121)	117(4)	454(4)	−209(4)
H(122)	16(4)	430(3)	−123(4)
H(131)	−164(4)	415(4)	−410(5)
H(132)	−134(4)	272(4)	−376(5)
H(133)	−32(4)	301(4)	−464(5)

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* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

ted for Lorentz and polarization factors, but no absorption correction was applied. The absolute scale and the mean temperature factor were determined by Wilson's method.

Structure Determination and Refinement.—The structure was solved by Patterson and Fourier methods and the refinement was carried out by full-matrix least-squares cycles using the SHELX system of programs [29] with initially isotropic and then anisotropic thermal parameters. A subsequent difference-Fourier map based on the above refinement showed the positions of all the hydrogen atoms. Further least-squares refinement including positional and isotropic thermal parameters for the hydrogen atoms was carried out. Unit weights were used at each stage of the refinement by analyzing the variation of ΔF as a function of $|F_o|$. Atomic scattering factors (corrected for the anomalous dispersion of Fe) were taken from ref. 30. The final R value was 0.027 (observed reflections only). Final atomic co-ordinates are given in Table 1; thermal parameters of the atoms and a list of calculated and observed structure factors are available from the authors on request or as Supplementary Publication No. SUP 22445 (19 pp.).*

All the calculations were carried out on a Cyber 76 computer of Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna).

DISCUSSION

Structure of the Complex.—The structure of (**1**) is represented in Figure 1; the bond distances and angles not involving hydrogen atoms are given in Table 2. The complex is formed by two non-equivalent Fe atoms, both co-ordinated by three terminal CO groups, and by a diethyl-substituted 'acrylate' ligand bound to both Fe atoms *via* Fe–C π and Fe–C and Fe–O σ bonds. This acrylate group is derived from the insertion of a CO_2 group between the alkyne and the metal atoms. A π-donor bond is formed by the C(7)–C(8) double bond of the organic ligand with Fe(1) which is also σ-bonded to O(7) of the carboxyl group. The other iron atom Fe(2) is σ-bonded to the carbon C(7) of the alkyne and to O(7); the latter atom is thus bound to both Fe atoms by a nearly symmetrical bridge [Fe(1)–O(7) 1.990(4) and Fe(2)–O(7) 1.950(4) Å]. By considering the organic ligand as a six-electron donor to the $Fe_2(CO)_6$ core the effective atomic number rule is satisfied. The Fe(2), O(7), C(9), C(8), and C(7) atoms participate in the formation of a a five-membered heterocyclic ring. This very unusual heterocycle, presented in Figure 2, is, to our knowledge, the first example of its type. The heterocycle is not planar, the equation of the mean plane passing through the atoms of the ring being $-0.3075X -0.4672Y - 0.8290Z = -1.1529$.† Fe(2), O(7), C(7), C(8), and C(9) are displaced from this plane by 0.019,

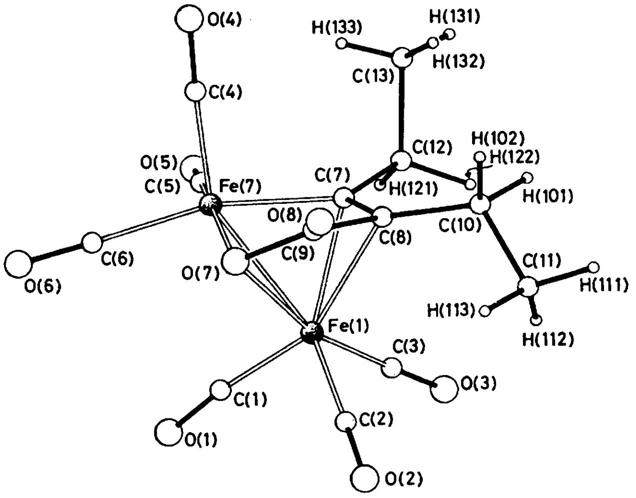

FIGURE 1 Perspective view showing the molecular shape and the atomic numbering

TABLE 2

Bond distances (Å) and angles (°) (not involving hydrogen atoms) with their estimated standard deviations

(*a*) In the co-ordination sphere of the iron atoms

Fe(1)–Fe(2)	2.438(3)	Fe(1)–C(8)	2.155(5)
Fe(1)–O(7)	1.990(4)	Fe(2)–O(7)	1.950(4)
Fe(1)–C(1)	1.790(6)	Fe(2)–C(4)	1.785(4)
Fe(1)–C(2)	1.820(4)	Fe(2)–C(5)	1.777(6)
Fe(1)–C(3)	1.769(5)	Fe(2)–C(6)	1.834(6)
Fe(1)–C(7)	2.092(4)	Fe(2)–C(7)	1.952(6)

Fe(2)–Fe(1)–O(7)	51.0(1)	C(3)–Fe(1)–C(7)	89.2(1)
Fe(2)–Fe(1)–C(1)	80.1(1)	C(3)–Fe(1)–C(8)	100.5(1)
Fe(2)–Fe(1)–C(2)	147.2(1)	C(7)–Fe(1)–C(8)	38.5(1)
Fe(2)–Fe(1)–C(3)	119.7(1)	Fe(1)–Fe(2)–O(7)	52.5(1)
Fe(2)–Fe(1)–C(7)	50.3(1)	Fe(1)–Fe(2)–C(4)	138.8(1)
Fe(2)–Fe(1)–C(8)	75.4(1)	Fe(1)–Fe(2)–C(5)	112.1(1)
O(7)–Fe(1)–C(1)	96.8(1)	Fe(1)–Fe(2)–C(6)	109.3(1)
O(7)–Fe(1)–C(2)	97.3(1)	Fe(1)–Fe(2)–C(7)	55.6(1)
O(7)–Fe(1)–C(3)	165.2(1)	O(7) Fe(2)–C(4)	99.7(1)
O(7)–Fe(1)–C(7)	76.1(1)	O(7)–Fe(2)–C(5)	163.9(1)
O(7)–Fe(1)–C(8)	67.1(1)	O(7)–Fe(2)–C(6)	90.1(1)
C(1)–Fe(1)–C(2)	98.1(1)	O(7)–Fe(2)–C(7)	80.4(1)
C(1)–Fe(1)–C(3)	92.1(1)	C(4)–Fe(2)–C(5)	95.9(1)
C(1)–Fe(1)–C(7)	121.9(1)	C(4)–Fe(2)–C(6)	99.2(1)
C(1)–Fe(1)–C(8)	155.5(1)	C(4)–Fe(2)–C(7)	94.0(2)
C(2)–Fe(1)–C(3)	93.1(2)	C(5)–Fe(2)–C(6)	91.6(2)
C(2)–Fe(1)–C(7)	139.8(2)	C(5)–Fe(2)–C(7)	94.5(2)
C(2)–Fe(1)–C(8)	102.1(2)	C(6)–Fe(2)–C(7)	164.9(2)

(*b*) In the carbonyl groups

O(1)–C(1)	1.132(6)	O(4)–C(4)	1.127(4)
O(2)–C(2)	1.123(5)	O(5)–C(5)	1.142(6)
O(3)–C(3)	1.142(6)	O(6)–C(6)	1.126(6)

Fe(1)–C(1)–O(1)	173.3(3)	Fe(2)–C(4)–O(4)	177.2(4)
Fe(1)–C(2)–O(2)	177.8(4)	Fe(2)–C(5)–O(5)	179.2(4)
Fe(1)–C(3)–O(3)	178.5(4)	Fe(2)–C(6)–O(6)	178.4(3)

(*c*) In the organic ligand

C(9)–O(7)	1.373(5)	C(8)–C(9)	1.473(5)
C(9)–O(8)	1.202(5)	C(8)–C(10)	1.507(6)
C(7)–C(8)	1.402(5)	C(10)–C(11)	1.491(6)
C(7)–C(12)	1.519(6)	C(12)–C(13)	1.523(6)

C(9)–O(7)–Fe(1)	89.4(2)	C(9)–C(8)–Fe(1)	80.7(2)
C(9)–O(7)–Fe(2)	113.2(2)	C(7)–C(8)–C(9)	113.3(3)
Fe(1)–O(7)–Fe(2)	76.5(1)	C(10)–C(8)–Fe(1)	131.5(2)
C(8)–C(7)–C(12)	121.4(3)	C(10)–C(8)–C(7)	127.5(3)
C(8)–C(7)–Fe(1)	73.2(2)	C(7)–C(8)–Fe(1)	68.3(2)
C(8)–C(7)–Fe(2)	113.2(2)	O(7)–C(9)–O(8)	122.5(3)
C(12)–C(7)–Fe(1)	128.9(2)	O(7)–C(9)–C(8)	107.5(3)
C(12)–C(7)–Fe(2)	124.6(2)	O(8)–C(9)–C(8)	129.9(3)
Fe(1)–C(7)–Fe(2)	74.1(1)	C(11)–C(10)–C(8)	115.8(4)
C(9)–C(8)–C(10)	117.6(3)	C(13)–C(12)–C(7)	111.2(3)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

† X, Y, and Z are orthogonal co-ordinates (Å) obtained from the fractional ones by applying the matrix $||a\sin\gamma, 0, -c\sin\alpha\cos\beta^{*}|\, a\cos\gamma, b, c\cos\alpha|0,0,c\sin\alpha\sin\beta^{*}||$.

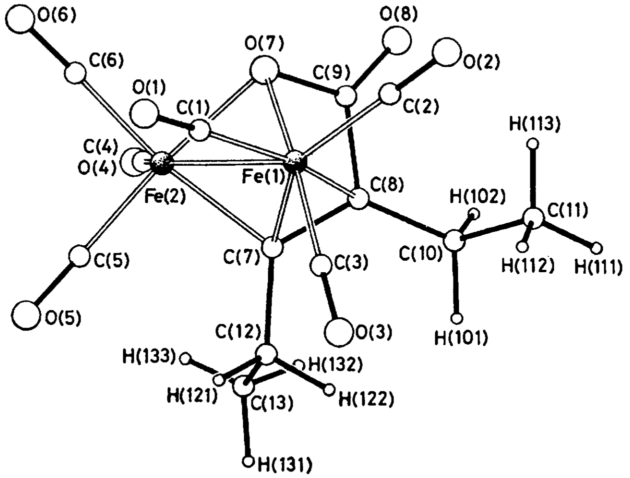

FIGURE 2 Bonding of the organic ligand to the two Fe atoms, with formation of a five-membered heterocyclic ring

—0.196, —0.120, —0.009, and 0.306 Å respectively. The carbon atoms C(10), C(8), C(7), and C(12) are perfectly coplanar and the equation of the mean plane passing through them is $-0.2266X - 0.4265Y - 0.8756Z = -0.8809$; C(12), C(7), C(8), C(10), C(9), O(7), O(8), Fe(2), and Fe(1) are displaced from this plane by —0.001, 0.002, —0.003, 0.002, 0.342, —0.031, 0.796, 0.310, and 1.620 Å respectively.

The Fe–Fe distance [2.438(3) Å] is one of the shortest found in binuclear derivatives of the iron carbonyls; normally distances in the range 2.50—2.70 Å are found.[31] Exceptions to this behaviour have been reported in binuclear derivatives substituted with $C_2Bu^t_2$,[32,33] where Fe–Fe distances of 2.316 and 2.215 Å were found in the mono- and di-substituted derivative respectively, but in these complexes the existence of multiple Fe–Fe bonding was proposed. An Fe–Fe distance of 2.46 Å was reported for $[Fe_2(CO)_9]$ which is characterized by three CO bridges.[31] Considerable Fe–Fe bond shortening (2.372 Å) has also been observed[34] in a bis(tricarbonyliron) complex containing nitrogen bridges comparable to the present oxygen bridge. The rather short Fe–Fe distance in the present complex could be due both to the organic bridge and particularly to the bite size of the oxygen O(7). A longer Fe–Fe distance [2.532(3) Å] was found in the closely related complex $[Fe_2(CO)_6(C_2H_2COS)]$,[35] prepared from $[Fe(CO)_5]$ and thiomaleic anhydride; the lengthening of the distance with respect to our complex can be ascribed to the larger bite size of the sulphur than oxygen.

In the carboxyl group the C(9)–O(7) distance [1.373(5) Å] corresponds to an elongated double bond whereas C(9)–O(8) [1.202(5) Å] is close to the C=O double bond found in carboxylic acid derivatives. The three-co-ordinate oxygen O(7) forms angles of 76.5(1), 89.4(1), and 113.2(1)° with the metals and C(9), Fe(1)–O(7)–Fe(2) and Fe(1)–O(7)–C(9) being narrower than those expected for sp^3 hybridization of oxygen; this distortion is probably due to the necessity for O(7) to bridge the metal atoms and to participate in the formation of the five-atom ring with Fe(2). A similarly co-ordinated oxygen atom has been found in $[Fe_4(CO)_{11}(NEt)(ONEt)]$.[36,37]

In the present complex a considerable lengthening of the former $C\equiv C$ triple bond of the alkyne is observed, the C(7)–C(8) distance being 1.402(5) Å, typical of a bond order of 1.5. The Fe(2)–C(7) distance is comparable with other Fe–C σ bonds.[4-6]

Carbon-13 *N.M.R. Studies*.—The room-temperature ^{13}C n.m.r. spectrum (^{1}H-decoupled) of the complex shows eight absorptions at 206.6, 190.7, 170.0, 109.0, 36.4, 21.4, 17.0, and 15.7 p.p.m. relative to $SiMe_4$. The high-field resonances are easily assigned to two different ethyl groups, and the lowest-field broad resonance can be attributed to the six exchanging carbonyls. The three remaining signals are assigned as follows, on the

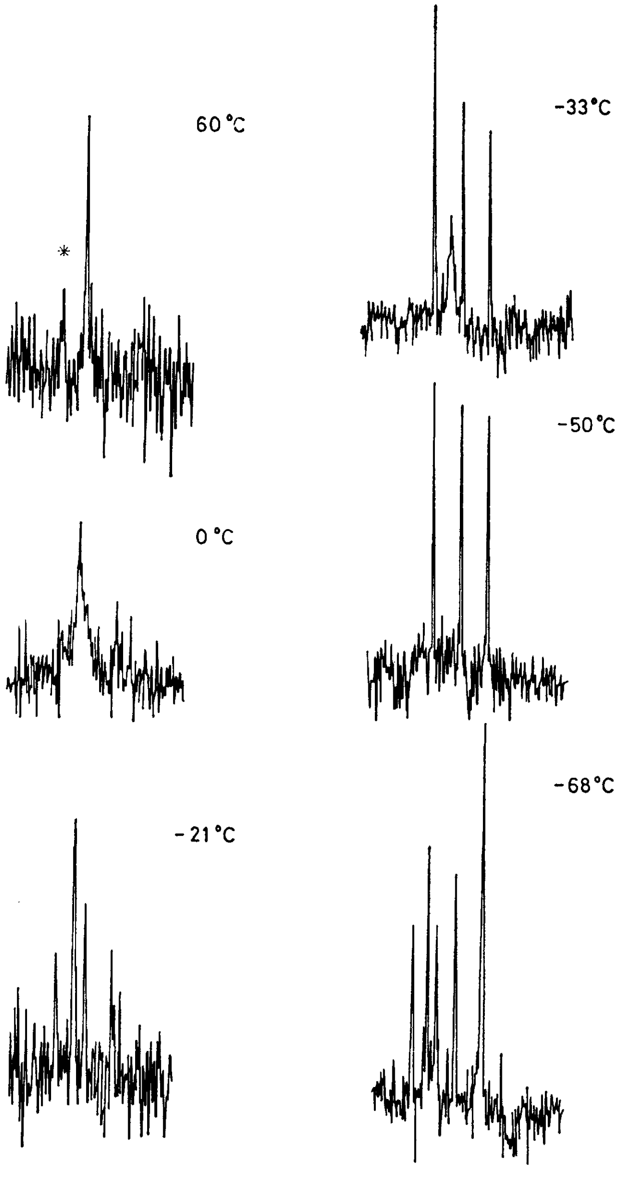

FIGURE 3 Variable-temperature ^{13}C spectra of complex (1) in the carbonyl region. The asterisk indicates an impurity due to the incipient decomposition of the sample

basis of the residual coupling observed in the undecoupled spectrum and of their position: the signals at 190.7 and 109.0 p.p.m. respectively to C(7) and C(8); the resonance at 170.0 p.p.m. to C(9). In Figure 3 are shown the variable-temperature ^{13}C n.m.r. spectra in the carbonyl region. At −68 °C the spectrum shows five resonances at 212.2, 210.0, 208.7, 205.9, and 202.0 p.p.m. in the intensity ratio (from low to high field) of 1 : 1 : 1 : 1 : 2. Casual superimposition of the signals of the two non-equivalent CO groups is likely to account for the peak of intensity 2 as confirmed by the behaviour of the resonances at higher temperatures. Thus, the resonances at 212.2, 208.7, and 202.0 p.p.m. first broaden and the two low-field ones disappear at −50 °C; at this temperature the resonances at 210.0, 205.9, and 202.0 p.p.m. (now of intensity 1) remain sharp. These observations can be accounted for by localized scrambling of the CO groups at one of the $Fe(CO)_3$ units. At −10 °C the other resonances which were previously unaffected broaden and collapse. Finally, at room temperature the spectrum shows only a broad absorption, which sharpens at higher temperatures. In this range of temperature some decomposition of the complex takes place. The observation of a single peak at 60 °C indicates that all the carbonyls are now equivalent on the n.m.r. time scale.*

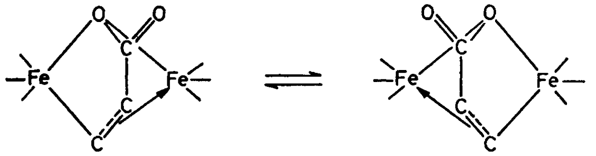

FIGURE 4 Proposed flipping of the organic moiety at greater than room temperature

Scrambling of the carbonyl groups in binuclear iron derivatives, not having bridging CO, is uncommon. Exceptions have been reported for derivatives having the metal carbonyl groups bonded to a polyene or a polyenyl group.[38] Thus, although delocalized carbonyl exchange cannot be ruled out, we feel that the flipping of the organic moiety as shown in Figure 4 is likely to account for the observed dynamic behaviour. A similar fluxional process has recently been reported for the vinyltriosmium derivatives $[Os_3(CO)_{10}(CH=CHR)H]$.[39]

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* *Note added at proof:* An analogous dynamic behaviour has been reported for the closely related complex $[Fe_2(CO)_6(C_2Ph_2S)]$ (J. P. Hickey, J. C. Huffman, and L. J. Todd, *Inorg. Chim. Acta*, 1978, **28**, 77).